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KANSAS UNIV LAWRENCE DEPT OF CHEMISTRY
LABORATORY STUDIES OF SOLVATED GAS-PHASE ANIONS.(U)
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FINAL SCIENTIFIC REPORT

TITLE: Laboratory Studies of Solvated Gas-Phase Anions

PRINCIPAL INVESTIGATOR: Professor Peter M. Hierl
Department of Chemistry
University of Kansas
Lawrence, Kansas 66045

INCLUSIVE DATES: 1 March 1981 - 28 February 1982

GRANT NUMBER: AFOSR-81-0105

COSTS AND FY SOURCE: \$9,944, FY 82 (MINI GRANT)

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A. RESEARCH OBJECTIVES

The objective of this research project was the study of the gas-phase reactions of solvated anions such as $\text{OH}^{\cdot-} \cdot n\text{H}_2\text{O}$ (where n ranges from 0 to 6) with neutral molecules of atmospheric interest such as CO_2 or SO_2 . These reactions, which include solvent switching, electron transfer, proton transfer, isotope exchange, and collision-induced dissociation, are important in predicting the composition of the Earth's atmosphere subsequent to natural and artificial perturbations such as aurora, nuclear detonation, and missile reentry. Improved knowledge of this subject is necessary for better detection and tracking of spacecraft and post boost vehicles.

More specifically, this project had the following objectives:

(1) The processing of kinetic data collected at the Air Force Geophysics Laboratory, where the Principal Investigator spent ten weeks during the summer of 1980 as an AFOSR Summer Faculty Research Program participant.

(2) The analysis and interpretation of the processed kinetic data. For the exothermic solvent switching reactions, this involves the comparison of the measured reaction rates with calculated rates derived from current theories of ion-molecule reaction and, when possible, with rates measured in other laboratories. For the endothermic collisional dissociation processes, this involves the analysis of the energy-dependence of the reaction cross section near threshold to obtain information on the bond strengths and the structures of the ions undergoing dissociation.

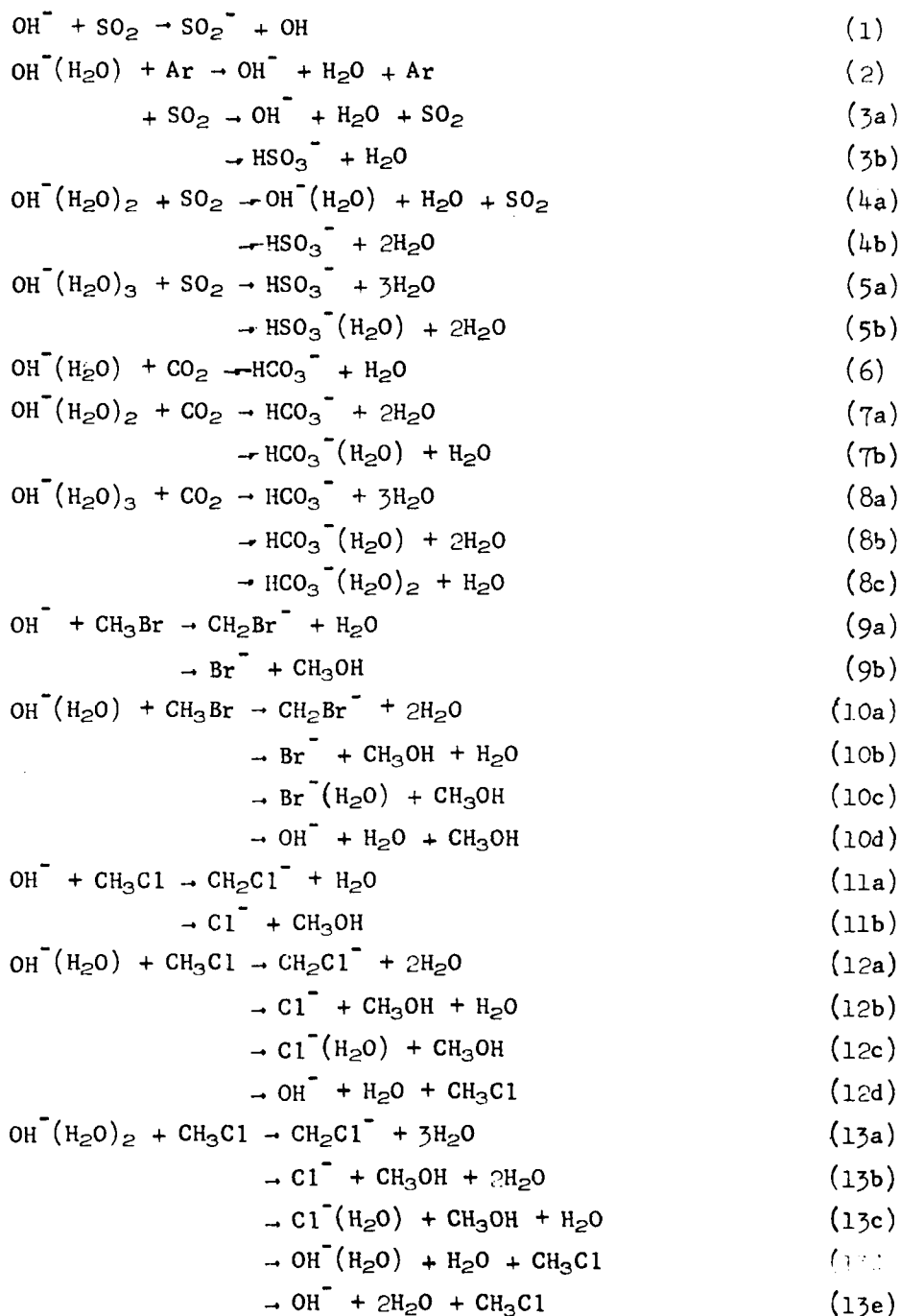
(3) The development of new ion sources capable of producing intense, monoenergetic beams of cluster ions of the type $\text{OH}^{\cdot-} \cdot n\text{H}_2\text{O}$, where n extends up to 5 or 6, and of mixed clusters such as $\text{HCO}_3^{\cdot-} \cdot n\text{H}_2\text{O}$.

B. STATUS OF THE RESEARCH

(1) Processing of kinetic data

During the ten week period the Principal Investigator spent at the Air Force Geophysics Laboratory, kinetic data were collected for the following reactions:

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Typically, data for a particular reaction were obtained for 2 to 5 replicate runs in which the reactant and product ion intensities [$I^+(\text{A}^-)$ and $I(\text{C}^-)$, respectively] were measured at each of 30 to 50 selected col-

lision energies covering the range 0.15 to 25 eV (LAB).

Data processing, which was completed during the period covered by this report, consisted of the following steps:

(a) Correcting the intensities $I^{\circ}(A^-)$ and $I(C^-)$ measured in a given run for any possible differences in the transmission efficiency of the quadrupole mass spectrometer employed to detect the ions A^- and C^- .

(b) Correcting the observed intensities $I^{\circ}(A^-)$ for those ions arriving at the detector during the "dead time" of the pulse counting system.

(c) In the studies of collisional dissociation, correcting the observed rate for the effect of collisions with molecules of background gas.

(d) Averaging the results of the replicate runs for each particular reaction.

(e) Plotting the averaged cross sections for each reaction versus the relative translational energy of the reactants to produce plots of what are known as excitation functions for each reaction.

(2) Data Analysis and Interpretation

(a) The dependence of the reaction cross section σ on the reactants' relative translational energy E_T was determined for the various exothermic reactions by plotting $\log \sigma$ vs. $\log E_T$. Such plots usually showed a linear dependence at low collision energies (E_T less than 1 eV), a curved transition region at intermediate energies (1-2 eV), and a second linear region at higher energies. Thus, in the limit of low or high energy, the dependence of the reaction cross section on collision energy can be expressed as $\sigma(E_T) \propto E_T^{-s}$, where the parameter s , determined from the slopes of the linear portions of these log-log plots, usually has a value of about 0.5 at low energy and a value of 5-7 at high energy.

(b) The cross sections measured at a particular collision energy E_T were converted to monoenergetic rate coefficients $k(E_T)$ by the relation $k(E_T) = v_r \sigma(E_T)$, where v_r is the relative velocity between the reactants corresponding to a relative translational energy E_T . Quasi thermal energy rate coefficients were then obtained by extrapolating the derived monoenergetic rate coefficients to thermal energy.

The exothermic solvent switching reactions between $\text{OH}^-(\text{H}_2\text{O})_n$ and CO_2 and SO_2 were found to be very rapid; the derived thermal energy rate coefficients were on the order of $1\text{--}3 \times 10^{-9} \text{ cm}^3/\text{molecule-sec}$, suggesting that reaction occurs on every or nearly every collision between the reactants. Increasing the degree of solvation of the reactant $\text{OH}^-(\text{H}_2\text{O})_n$ ion was found to have no effect on the rate of the reaction with SO_2 , and only slightly decreased the rate of the reaction with CO_2 .

Theoretical rate coefficients for these solvent switching reactions were calculated from several current models for ion-molecule reactions. The AADO theory of Su, Su and Bowers [T. Su, E.C.F. Su, and M.T. Bowers, J. Chem. Phys. 69, 2245 (1978)] predicted rate coefficients which were within a factor of two of those measured in the present study. Moreover, this model successfully predicted that SO_2 would react more rapidly with $\text{OH}^-(\text{H}_2\text{O})_n$ than does CO_2 because the permanent dipole moment of SO_2 enhances the long-range attractive forces and thus the frequency of collisions (CO_2 is non-polar).

One interesting observation made in this study was the fact that the major products of the solvent switching reactions are the unsolvated ion HCO_3^- and HSO_3^- , even when the reactant ion was $\text{OH}^-(\text{H}_2\text{O})_3$. This failure of the water molecules to solvate the ionic product (thus forming energetically more favorable products) we attribute to the high exothermicity of these reactions. Because the OH^- - SO_2 and OH^- - CO_2 bond energies are much greater than the OH^- - H_2O bond energy, sufficient energy is released in these switching reactions to cause the decomposition of any solvated ionic products via "solvent boil-off".

In analyzing the data on the collisional dissociation processes, we had to take into account the thermal motion of the target molecules because such motion tends to smear out the onset of dissociation at collision energies above threshold due to the Doppler effect. This was done by assuming a functional form for the true microscopic reaction cross section, convoluting this assumed function with the experimental conditions, and then comparing the calculated results with the phenomenological cross sections.

We assumed that the true cross sections $\sigma(E_T)$ for these endothermic processes increase linearly with relative translational energy E_T above the

threshold value E_0 according to the equation

$$\sigma(E_T) = \begin{cases} 0 & \text{if } E_T < E_0 \\ Q(E_T - E_0) & \text{if } E_T \geq E_0 \end{cases}$$

Assuming that a monoenergetic ion beam interacts with target gas molecules having an isotropic Maxwellian velocity distribution, we have convoluted the assumed cross section with the distribution in relative velocities according to the procedure described by Chantry [P.J. Chantry, J. Chem. Phys. 55, 2746 (1971), Eq. (30)]. The results were then compared with the phenomenological cross sections, and the parameters Q and E_0 were varied until satisfactory agreement was achieved.

Agreement between the calculated excitation function and the measured cross sections was generally very good, indicating (1) a linear excitation function above threshold is adequate to describe the energy dependence of the cross section for the collision-induced processes, and (2) our reactant ions possessed little if any internal excitation which, if present, would have caused more tailing than observed in the measured cross sections at energies below threshold.

The threshold energies correspond to the dissociation energy of the bond being broken in the dissociation process. Values of 1.12 ± 0.10 eV and 0.80 ± 0.10 eV were obtained for the dissociation of $\text{OH}^- - \text{H}_2\text{O}$ and $\text{OH}^-(\text{H}_2\text{O}) - \text{H}_2\text{O}$, respectively, in very good agreement with values obtained in other laboratories employing different methods. Moreover, we obtained a value of 3.8 ± 0.25 eV for the $\text{OH}^- - \text{CO}_2$ bond dissociation. Since such a high value indicates appreciable chemical bonding (as opposed to simple electrostatic attraction), we have chosen to write this ion as HCO_3^- rather than as $\text{OH}^-(\text{CO}_2)$. Our observation that SO_2 rapidly reacts with HCO_3^- to produce HSO_3^- indicates that the reaction is exothermic and therefore that the bond dissociation energy of $\text{OH}^- - \text{SO}_2$ is greater than 3.8 eV.

Manuscripts describing these results in more detail have been prepared for publication, and copies will be forwarded to the AFOSR in the near future.

(3) Ion Source Design

Attempts were initiated to design and construct ion sources capable of

producing intense, monoenergetic beams of cluster ions such as $\text{OH}^-(\text{H}_2\text{O})_n$, where n extends up to 5 or 6. Unfortunately, only preliminary results have been obtained during the period of this project. These preliminary results, however, have served to identify the problems that must be overcome in the design of such an ion source.

The kinetics of the three-body association reactions leading to cluster formation are sufficiently well known that appropriate source conditions can be calculated. The source must operate at gas pressures of up to 1 Torr, and the ions should have a residence time of at least several microseconds in the source. (Although it is possible to compensate for lower pressures with longer residence times, this trade-off is unfavorable, since a ten-fold decrease in pressure would require a hundred-fold increase in residence time.)

By using field-penetration from an extraction plate in front of the ion source rather than a repeller plate within the source, we have been able to form thermal-energy ions whose residence time in the source exceeds several microseconds.

Operating an ion source at pressures of 1 torr, however, creates at least three problems. (1) Because of the great pressure differential between the source and the surrounding vacuum system, the source must be very "tight" and high speed vacuum pumps must be available. However, such tight sources are commonly used in chemical ionization mass spectrometry, so the problem here is one of optimizing the design of such ion sources. (2) Because the ionizing electron beam is rapidly attenuated at high gas pressures, adequate penetration of the beam from an external filament into the source can present a problem. We are currently investigating the possibility of using a very high energy electron beam which, upon collisions with the source wall or the gas within the source, will eject secondary electrons that actually cause the desired ionization. (3) The large voltage difference between the ion source and the gas inlet system produces a discharge through the gas inlet line when the gas pressure in the line approaches 1 Torr. Again, there are known to be several solutions to this problem, and we are currently investigating them.

C. PUBLICATIONS

1. John F. Paulson and Peter M. Hierl, "Translational Energy Dependence of Cross Sections for Reactions of $\text{OH}^-(\text{H}_2\text{O})_n$ with CO_2 and SO_2 ," manuscript in final stages of preparation for submission to The Journal of Chemical Physics.
2. John F. Paulson, Michael J. Henchman, and Peter M. Hierl, "Effect of Reactant Ion Solvation on Gas-Phase $\text{S}_\text{N}2$ Reactions," manuscript in final stages of preparation for submission to The Journal of Chemical Physics.

D. PROFESSIONAL PERSONNEL

Calvin Cole, Ph.D. Candidate, Department of Chemistry, University of Kansas, Lawrence, KS 66045

E. INTERACTIONS

1. Oral Presentations

P.M. Hierl, M.J. Henchman, and J.F. Paulson, "Tandem Mass Spectrometric Studies of the Reactions of Solvated Anions," presented at the 29th Annual Conference on Mass Spectrometry and Allied Topics, Minneapolis, Minnesota, May 24-29, 1981.

2. Consulting - none

F. NEW DISCOVERIES, INVENTIONS

none

